Synthesis and transport properties of phosphorylated polyvinyl alcohol membranes for redox Fe^{3+}/H_2 flow cell

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Fuel cells redox flow batteries are used in the electrochemical energy conversion and electrical energy storage technologies [1–3]. A hybrid Fe^{3+}/H_2 redox flow system is very promising among those and the polyvinyl alcohol-based membranes are believed to be components of this system.

A novel method for preparation of phosphorylated polyvinyl alcohol (p-PVA) membranes was developed and used to synthesize a series of membranes with different degree of phosphorylation (4–9 w. % of phosphorus). The optimal mass ratio of PVA : H_3PO_2 was found to be 4 : 1, while the optimal curing time was 3 h at a temperature of 120 ^oC. The membranes possessed good mechanical robustness and chemical stability in acidic media. A method, based on "diatomic approximation" and combined with the Badger's rule and Brown's bond valence concept, was developed to estimate the chemical bonds frequencies with an accuracy of $\pm$ 20–25 cm^{-1} and was used to interpret the IR-spectra of the membranes. The possibble pathway of PVA phosphorylation leading to formation of P–C bonds and various chemical functionalities was suggested.

The water flux ($6.08\cdot10^{-2}$ $g\cdot cm^{-2}\cdot h^{-1}$) and permeability of ferric ions ($3.5\cdot10^{-5}$ $cm^2\cdot min^{-1}$) were comparable to those of commercial Nafion 117 membrane. The dependence of the proton conductivity on the concentration of H_2SO_4 at 22 ^oC was studied and the intrinsic proton conductivity of the p-PVA membrane ($5.5\cdot10^{-3}$ $S\cdot cm^{-1}$) was determined. The partial charges on oxygen atoms in structural linkages were calculated and the results indicate on the Grotthuss mechanism of proton transport. The increased density of negative charges on oxygen atoms in structural linkages results in extra hydrogen bonding within the p-PVA matrix and affects not only proton conductivity, but also water flux trough the membrane and other transport properties. The doping of p-PVA membrane with $2NH_2SO_4$ increases the proton conductivity to the value close to the conductivity of commercial Selemion HSF membrane.

References

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